(12)   **EUROPEAN PATENT SPECIFICATION**

(54) **Components and catalysts for the polymerization of olefins**

Komponenten und Katalysatoren zur Polymerisation von Olefinen

Composants et catalyseur pour la polymérisation d'oléfines

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**EP-A- 0 395 083   EP-A- 0 423 861
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Description

The present invention relates to components of catalysts for the polymerization of olefins, the catalysts obtained therefrom and the use thereof in the polymerization of ethylene and mixtures thereof with α-olefins $CH_2=CHR$, where R is a hydrocarbon radical having from to 12 carbon atoms.

The need for having available in the industrial practice catalysts supported on magnesium dihalides in active form, endowed with a high activity and capable of providing polymers with a controlled morphology is more and more felt.

Examples of catalysts having a controlled morphology are described in US Patents 3,953,414 and 4,399,054. In the latter patent, the components are prepared from spherically shaped adducts of $MgCl_2$ with approximately 3 mols of alcohol. Prior to the reaction with $TiCl_4$, the alcohol content is decreased down to 2.5-2 mols: in this manner, components are obtained which exhibit a porosity, as measured with nitrogen, of from 0.3 to 0.4 g/cm^3 and an average pore radius comprised between 0.0015 and 0.0020 μm (15 and 20 Å).

Catalysts prepared from $TiCl_4$ and $MgCl_2$ in granular form, by spray drying an alcohol solution of magnesium chloride and subsequently supporting the titanium compound, are described in patents EP-B-65700 and EP-B-243327. However, the polymer obtained using these catalysts does not exhibit morphological characteristics of interest. In particular, the bulk density is not sufficiently high. Furthermore, the activity of the catalyst is rather low.

A method for increasing the activity of these catalysts is described in patent EP-A-281524. These catalysts are prepared by supporting titanium alkoxides onto an $MgCl_2$-ethanol adduct, containing from 18 to 25% by weight of ethanol, spherulized by spray-drying of an ethanol solution thereof and subsequent chemical treatment with Et_2AlCl or $Et_3Al_2Cl_3$. The conditions for preparing the support are critical and have an influence on the morphological stability of the resulting polymer. For example, polymers in the form of heterogeneous powder are obtained when supports are used having an alcohol content which is not comprised within the range of 18-25%, or compounds are used which are different from Et_2AlCl or $Et_3Al_2Cl_3$. Furthermore, in order to achieve high yields the Ti content in the solid component is always greater than 8% by weight.

From patent application EP-A-395083, catalysts suitable for producing spherically shaped polymers endowed with satisfactory morphological properties are known, obtained from $MgCl_2$-alcohol adducts, in which the adduct, generally containing 3 mols of alcohol per mol of $MgCl_2$, is dealcoholated by thermal treatment down to alcohol levels generally comprised between 0.2 and 2 mols, and is thereafter caused to react with an excess of titanium tetrachloride optionally containing an electron donor compound dissolved therein.

The solid components of these catalysts are characterized by a high specific surface area and microporosity (more than 50% of the pores has an average radius smaller than 0.08 μm).

When used for the polymerization of ethylene to produce LLDPE, these catalysts lead to a comonomer distribution which is not sufficiently uniform.

It has now been unexpectedly found that catalysts having a spherical shape can be obtained, which are capable of leading to a uniform comonomer distribution in the preparation of LLDPE, and in general in the preparation of copolymers endowed with interesting morphological properties, in particular polymers having a high bulk density when obtained by polymerization in the gas phase, notwithstanding the significant macroporosity of the solid components forming the catalyst.

The spherical components of the invention comprise, supported on a magnesium dihalide in active form, a titanium compound containing at least one Ti-halogen bond and one OR or OCOR group, wherein R is an alkyl or cycloalkyl or aryl radical of 1-18 carbon atoms, said OR or OCOR group being bonded to the titanium atom in such an amount as to yield molar ratios OR/Ti which are greater than or equal to 0.5; optionally, an electron donor compound can also be present.

Said components are characterized by having a porosity comprised between 0.35 and 0.7 cm^3/g, and by a pore size distribution such that at least 50% of the porosity is due to pores having an average radius greater than 0.08 μm (800 Å). Their specific surface area is generally comprised between 5 and 30 m^2/g.

The porosity values indicated above refer to measurements carried out on pores having a radius of up to 1 μm (10,000 Å).

The spherical components of the invention are furthermore characterized in that at least 30% of the total porosity is due to pores having a radius greater than 1 μm (10,000 Å). As defined herein the total porosity refers to measurements carried out on pores having a radius comprised between 0 to 30 μm (300,000 Å).

The porosity and specific surface area are determined by mercury porosimetry, according to the method hereinafter described.

The magnesium dihalides in active form comprised in the spherical component of the invention are characterized by X-ray spectra wherein the most intense diffraction line appearing in the spectrum of the non-active halide shows a decreased intensity, and in said spectrum a halo appears, the maximum intensity of which is shifted towards lower angles with respect to the angles of the most intense line.

The particles have a spherical or spheroidal shape with an average diameter comprised between 10 and 150 μm. By particles having a spheroidal shape those particles are meant in which the ratio of the major axis to the minor axis is equal to or smaller than 1.5 and preferably smaller than 1.3.

Preferred titanium compounds have the formula Ti

$(OR^l)_nX_{y-n}$, wherein n is a number greater than or equal to 0.5 and is one unit less than the titanium valency y, and is preferably comprised between 1 and 2 when y is 4; X is halogen and R^l is an alkyl radical of 2-8 carbon atoms, in particular n-butyl, isobutyl, 2-ethylhexyl, n-octyl and phenyl.

The titanium compound to be supported onto the magnesium dihalide can be pre-formed, or it is produced in-situ by the reaction of a titanium tetrahalide, in particular $TiCl_4$, with the OH groups of the residual Alcohol present in a combined form in said magnesium dihalide, or by the reaction of said tetrahalide with alcohols ROH or with titanium alkoxides having the formula $Ti(OR)_4$.

The titanium tetralkoxides can furthermore be caused to react with halogenating compounds such as, for instance, SiC14, $AlCl_3$, chlorosilanes, Al-alkyl halides. In the latter case, the titanium valency is reduced and titanium haloalkoxides are formed wherein the titanium valency is lower than 4.

Titanium haloalkoxides with a valency lower than 4 can also be formed by means of the reaction of titanium tetralkoxides with mixtures of halogenating and reducing compounds.

The spherical catalyst components according to the present invention can be obtained by the reaction of:

(a) an $MgCl_2 \cdot pROH$ adduct, wherein p≤0.5 and R is an alkyl, cicloalkyl or aryl radical having 1-12 carbon atoms; with

(b) a titanium compound of the formula $Ti(OR)_nX_{4-n}$ or $Ti(OCOR)_nX_{4-n}$, wherein 0≤n≤2,

X is halogen and R is an alkyl, cicloalkyl or aryl radical having 1-18 carbon atoms; said adduct (a) being prepared by chemical dealcoholation of adducts $MgCl_2$. mROH, with m≤2, in turn obtained by thermal dealcoholation of adducts $MgCl_2 \cdot qROH$, wherein 2.5≤q≤3.5. Alternatively, the spherical catalyst components according to the present invention can also be obtained by the reaction of:

(a) an $MgCl_2 \cdot pROH$ adduct, wherein p≤0.5 and R is an alkyl, cicloalkyl or aryl radical having 1-12 carbon atoms; with

(b) a titanium compound of the formula $Ti(OR)_nX_{4-n}$ or $Ti(OCOR)_nX_{4-n}$, wherein 2≤n≤4, X is halogen and R is an alkyl, cicloalkyl or aryl radical having 1-18 carbon atoms;

(c) a halogenating compound, optionally in combination with a reducing compound, or a compound having both a halogenating and a reducing activity;

said adduct (a) being prepared by chemical dealcoholation of adducts $MgCl_2$.mROH, with m≤2, in turn obtained by thermal dealcoholation of adducts $MgCl_2$. qROH, wherein 2.5≤q≤3.5.

The titanium alkoxides to be used in the preparation of the catalyst component can be in the form of complexes with magnesium halides. Examples of the preparation of said complexes are given in US patent 4,218,339, the description thereof being herein incorporated by reference.

The magnesium dihalide in active form, preferably magnesium dichloride, is obtained from adducts $MgX_2 \cdot nROH$, wherein R is an alkyl or cycloalkyl or aryl radical of 1-12 carbon atoms and n is generally larger than 2 and in particular comprised between 2.5 and 3.5.

These adducts are prepared in spherical form from melted adducts, by emulsifying the adducts in a liquid hydrocarbon and thereafter causing them to solidify by fast quenching. A typical method for preparing these spherulized adducts is reported in US patent 4,469,648. According to said method, spheroidal adducts are obtained by mixing the molten adduct with at least one other liquid imiscible therewith and chemically inert thereto and in a ratio such that the molten adduct forms the dispersed phase and the liquid mixed therewith forms the continuous phase, subjecting the mixture to turbolent flow to obtain an emulsion, quenching the emulsion to solidify the dispersed phase and collecting the initially molten adduct in the form of solid, spheroidal particles resulting from the quenching. The thus obtained spherulized adducts are subjected to thermal dealcoholation at temperature comprised between 50 and 150 °C until the alcohol content is reduced to values lower than 2 and preferably comprised between 1.5 and 0.3 mols per mol of magnesium dihalide, and are finally treated with chemical reagents capable of reacting with the OH groups of the alcohol and of further dealcoholating the adduct until the content is reduced to values which are generally lower than 0.5 mols.

When the thermally dealcoholated adduct shows an alcohol content of around 2 mols, the content of residual alcohol may be up to 0.5 mols; preferably it is about 0.2-0.3 mols. Lower values are reached when the starting adduct contains a lower amount of alcohol.

The adducts can also be dealcoholated to a very great extent, by reducing the alcohol content down to values lower than 0.05 mols.

The treatment with the dealcoholating chemical agents is carried out by using an amount of such an agent which is large enough to react with the OH groups present in the alcohol contained in the adduct. Preferably, the treatment is carried out using a slight excess of said agent, which is then removed prior to the reaction of the titanium compound with the thus obtained support.

In the event that the chemical dealcoholation of the $MgCl_2 \cdot pROH$ adduct is carried out by using agents having a reducing activity, for instance an Al-alkyl compound such as Al-triethyl, the thus obtained compound, prior to the reaction with the titanium compound, can be treated with a deactivating agent, for instance O_2 or an alcohol, in order to deactivate the Al-triethyl possibly present therefore avoiding the reduction of the titanium compound.

The treatment with deactivating agents is avoided when one wishes to at least partially reduce the titanium compound. If on the other hand one wishes to reduce the titanium compound to a very great extent, the process for preparing the catalyst component can advantageously comprise the use of reducing agents.

The reaction with the titanium compound is carried out by using, as indicated above, the pre-formed haloalkoxide or halocarboxylate, or by forming said compound in-situ by reacting a Ti tetrahalide, in particular, $TiCl_4$, with the OH groups present in the adduct or with an alcohol ROH, or by causing a titanium tetralkoxide to react with a halogenating agent such as $SiCl_4$, halosilanes, $TiCl_4$ itself, $AlCl_3$, Al-alkyl halides.

In some instances it is convenient that the titanium compound be reduced to a valency lower than 4. Said result is obtained, for example, by using a halogenating agent which simultaneously acts as a reducing agent, such as, for instance, an Al-alkyl halide, or by using reducing agents such as silicon compounds, for instance polyhydrosiloxanes.

The amount of titanium compound used in the reaction corresponds to the amount which remains fixed on the support, or a slight excess is used; said excess is then removed.

In general, titanium is used in such an amount that the molar ratio Ti/Mg varies within the range of 0.05 to 3, and preferably within the range of 0.1 to 2.

The titanium amount which remains fixed on the support may reach, for instance, up to 15% by weight, expressed as the Ti metal content, and is preferably comprised between 1 and 12%.

The titanium compound supported on magnesium dihalide is fixed in a form which cannot be extracted by solvents; it may also be partially present in an extractable form.

The component of the invention may optionally comprise, in particular when one wishes to produce an LLDPE having a particularly narrow molecular weight distribution, also an electron donor compound (inside donor), e.g. a compound selected from ethers, esters, amines and ketones.

In particular, the electron donor compound can be selected from the alkyl, cycloalkyl and aryl esters of polycarboxylic acid, such as, for instance, esters of the phthalic and maleic acids, in particular n-butyl phthalate, diisobutyl phthalate di-n-octyl phthalate; other useful compounds are those disclosed in patent application EP-A-422755, in particular 2-methyl-2-isopropyl-1,3-dimethoxypropane 2-methyl-2-isobutyl-1,3-dimethoxypropane; 2-isopropyl-2-isopentyl-1,3-dimethoxypropane; 2,2-diisobutyl-1,3-dimetoxypropane.

The electron donor compound is generally present in a molar ratio to the magnesium of up to 1:2.

By reacting with Al-alkyl compounds, in particular Al-trialkyl compounds, the compounds of the invention form catalysts which, as already indicated, lead to a very uniform distribution of the comonomer along the polymer chain, and furthermore allow to obtain by polymerization in the gas phase polymers which are endowed with interesting morphological characteristics, in particular as regards the bulk density, which can be controlled up to very high values.

The evaluation of the comonomer distribution is carried out by measuring the polymer fraction which is soluble in xylene at 25°C, the content of bonded comonomer and the real polymer density.

The result obtained by polymerization in the gas phase is an all unpredictable result as regards the bulk density of the polymer, the range of which is shifted towards higher values than obtainable in the presence of a solvent.

Examples of an Al-alkyl compounds which can be used in the preparation of the catalyst are the Al-trialkyls, in particular Al-triethyl, Al-tri-n-butyl, Al-tri-isobutyl. The ratio Al/Ti is greater than 1 and generally comprised between 20 and 800.

The catalysts are advantageously used in the polymerization of ethylene and mixtures thereof with α-olefins $CH_2=CHR$, wherein R is an alkyl or cycloalkyl or aryl radical with 1-12 carbon atoms. In particular, they are used in the preparation of:

- high density polyethylenes (HDPE, having a density greater than 0.940 g/cm^3), including homopolymers of ethylene and copolymers of ethylene with alpha-olefins having from 3 to 14 carbon atoms;
- linear low density polyethylenes (LLDPE, having a density lower than 0.940 g/cm^3) and very low and ultra low density linear polyethylenes (VLDPE and ULDPE, having a density lower than 0.920 g/cm^3 and as low as 0.880 g/cm^3) consisting of copolymers of ethylene with one or more alpha-olefins having from 3 to 12 carbon atoms, having a content of units derived from ethylene greater than approximately 80% by weight;
- elastomeric copolymers of ethylene and propylene and elastomeric terpolymers of ethylene and propylene with minor amounts of a diene, having a content of units derived from ethylene comprised between about 30 and 70% by weight.

The polymerization of olefins in the presence of the catalysts obtained from the catalyst components of the invention can be carried out according to the known techniques both in the liquid phase and in the gas phase, by using, for example, the known fluidized bed technique or under conditions in which the polymer is stirred by mechanical means.

An example of a process in which the spherical components of the invention can be used is the process described in the International Patent Application WO 92/21706. Said process comprises a step of pre-contacting the catalyst components, a prepolymerization step, and a gas-phase polymerization step in two or more fluidized-bed or mechanically stirred-bed reactors

in series.

The following examples are supplied for merely illustrative purposes, and are not to be construed as being limitative of the invention itself.

The properties indicated are determined according to the following methods:

- <u>Porosity and specific surface area with nitrogen</u>: determined according to the B.E.T methodology (apparatus used SORPTOMATIC 1800 by Carlo Erba).
- <u>Porosity and specific surface area with mercury</u>: determined by immersing a known amount of sample in a known amount of mercury inside a dilatometer and then gradually increasing mercury pressure by a hydraulic means. The pressure of mercury entering the pores is a function of the diameter of the pores. The measurement is carried out by using a "Porosimeter 2000 Series" porosimeter by Carlo Erba. From the data of mercury volume decrease and of applied pressure, porosity, pore distribution and specific surface area are calculated.
- <u>Size of the catalyst particles</u>: determined according to a method based on the principle of optical diffraction of monochromatic laser light, using the "Malvern Instr. 2600" apparatus.
- <u>MIE flow index</u>:   ASTM-D 1238
- <u>MIF flow index</u>:   ASTM-D 1238
- <u>Flowability</u>: it is the time required by 100 g of polymer to flow through a funnel, the outlet opening thereof having a diameter of 1.25 cm, and the side walls being inclined at 20° to the vertical.
- <u>Bulk density</u>: DIN-53194
- <u>Morphology and Granulometric distribution of the polymer particles</u>:   ASTM-D 1921-63
- <u>Fraction soluble in xylene</u>: determined at 25°C.
- <u>Comonomer content</u>: percentage by weight, as determined via I.R. spectra.
- <u>Real density</u>:   ASTM-D 792.

EXAMPLES

PREPARATION OF THE SPHERICAL SUPPORT (MgCl₂/EtOH ADDUCT)

The adduct of magnesium chloride and alcohol was prepared according to the method described in Example 2 of US patent 4,399,054, but operating at 2,000 rpm instead of 10,000 rpm.

The adduct containing approximately 3 mols of alcohol had an average size of approximately 60 μm, with a dispersion range of approximately 30-90 μm.

EXAMPLE 1

Preparation of the Solid Component

The spherical support prepared according to the general method was subjected to thermal treatment, under nitrogen flow, within the temperature range of 50-150°C, until spherical particles having a residual alcohol content of about 35% (1.1 mols of alcohol per mol of $MgCl_2$) were obtained.

300 g of this support, in suspension with 3,000 cm^3 of anhydrous hexane, were charged to a 5,000 cm^3 reactor. With stirring and at ambient temperature, 130 g of $AlEt_3$ in solution in hexane (107 g/l) were slowly added. The temperature was raised to 60°C and kept constant for 60 minutes. Stirring was discontinued, settling was allowed to occur and the clear phase was removed. The treatment with $AlEt_3$ was repeated two more times under the same conditions. Then 3 washes with anhydrous hexane and drying at 50°C were carried out.

The thus obtained support exhibited the following characteristics:

- Porosity (Hg)   1.144 cm^3/g
- Surface Area (hg)   15.2 m^2/g
- Residual OEt   5.5 % (by weight)
- Residual Al   3.6 % (by weight)
- Mg   20.4 % (by weight)

260 g of the support were charged to a 1,000 cm^3 reactor together with 3,000 cm^3 of anhydrous hexane. Stirring was initiated and over a time period of 30 minutes 242 g of Ti(OBU)₄ were fed at ambient temperature. Stirring was continued for a further 30 minutes and then 350 g of $SiCl_4$ diluted with 250 cm^3 of hexane were fed over a 30 minute period and at ambient temperature. The temperature was raised to 65°C in 40 minutes and kept constant for 3 hours, then the liquid phase was separated out by settling and siphoning. Seven washes with hexane (3,000 cm^3 each time) were carried out, 3 thereof at 60°C and 4 at ambient temperature. The component in spherical form was vacuum dried at 50°C.

The characteristics were as follows:

- Total Titanium   3.4 % (by weight)
- Mg   17.1 % (by weight)
- Si   0.9 % (by weight)
- Cl   57.4 % (by weight)
- Residual Al   1.3 % (by weight)
- OEt   2.9 % (by weight)
- OBu   13.2 % (by weight)
- Porosity (B.E.T.)   0.108 cm^3/g, 50% thereof being due to pores with a radius of >0.035 μm (>350 Å)
- Surface Area (B.E.T.)   28.6 m^2/g
- Porosity (mercury)   0.536 cm^3/g due to pores with a radius of 0-to-1 μm (0-to-10,000 Å), 50% thereof being due to pores with a radius of >0.125 μm (>1,250 Å). Within the range of pores with a radius of 0-to-30 μm (0-to-300,000 Å), 48% of the pores had a radius of >1 μm (>10,000 Å)
- Surface Area (mercury)   12.8 m^2/g.

Copolymerization of Ethylene with Butene-1 (LLDPE)

A 4 liter stainless steel autoclave, purged under nitrogen flow for 2 hours at 70°C and then washed with anhydrous propane, was charged with 0.01 g of the solid component and 0.96 g of Al-trietyl mixed with 25 cm³ of hexane, and 800 g of anhydrous propane. The temperature was raised to 75°C, and then 2 bars of H_2 were fed simultaneously with 7 bars of ethylene and 200 g of butene-1.

During the course of polymerization, the ethylene partial pressure was kept constant and 3 g of butene-1 were added per each 30 g of ethylene fed. After three hours, the reaction was stopped by instantaneously venting off the reactants and propane. The produced amount of polymer was 280 g.

The characteristics of the polymer were as follows:

- MIE   0.99 g/10 min
- MIF/MIE   25.8
- Real Density   0.922 g/cm³
- Fraction Soluble in Xylene   7.5 %
- Bonded Butene   5.4 %
- Bulk Density, Poured   0.35 g/cm³
- Flowability   18 s
- Morphology   spherical
- P.S.D.   >4,000 μm   <0.5 % (by weight)
  2,000-4,000 μm   20-30 % (by weight)
  1,000-2,000 μm   40-70 % (by weight)
  500-1,000 μm   1-3 % (by weight)
  <500 μm   <1 % (by weight)

Polymerization of Ethylene (HDPE)

A 2.5 1 autoclave, purged as described above, was charged with 900 cm³ of hexane containing 0.45 g of $AlEt_3$ and 0.01 g of the spherical component suspended in 100 cc of the same $AlEt_3$/hexane mixture as described above. Stirring was initiated, the temperature was raised to 75°C, and then 3 bars of H_2 and 7 bars of ethylene were fed. The polymerization time was of 3 hours, during which time the ethylene pressure was kept constant. After 3 hours, the reaction was stopped by instantaneously venting off ethylene and hydrogen. 270 g of polymer were obtained, which exhibited the following characteristics:

- MIE   0.44 g/10 min
- MIF/MIE   28.8
- Real Density   0.961 g/cm³
- Bulk Density   0.32 g/cm³
- Flowability   18 s
- Morphology   spherical
- P.S.D.   >4,000 μm   <0.5 % (by weight)
  2,000-4,000 μm   20-30 % (by weight)
  1,000-2,000 μm   40-70 % (by weight)
  500-1,000 μm   2-4 % (by weight)
  <500 μm   <2 % (by weight)

EXAMPLE 2

The spherical support was prepared according to the general method and was subjected to thermal treatment followed by treatment with $AlEt_3$, according to the same methodologies described in Example 1. A 5 liter reactor was charged with 260 g of the thus obtained support, in suspension with 2.5 liters of anhydrous hexane. With stirring and at ambient temperature, 568 g of Ti $(OBu)_4$ were gradually fed. Stirring conditions were maintained at ambient temperature for 60 minutes and then 437 g of $SiCl_4$ diluted with 300 cm³ of hexane were fed over approximately 30 minutes and at ambient temperature. The temperature was then raised to 65°C and after 60 minutes was lowered to 40°C; at this point, 320 g of PMHS (polymethylhydrogensilane) were fed. The temperature was raised to 60°C and kept constant for 2 hours, with stirring. The solid catalyst component was then washed with hexane to eliminate any free $SiCl_4$, simultaneously taking care in removing a small amount of very fine powder (1-2%), of a size smaller than 5 μm, easily removed together with the wash liquids. The component was then vacuum dried at 50°C.

The characteristics were as follows:

- Total Titanium   4.5 % (by weight)
- Ti^{III} 2.2 % (by weight)
- Mg   15 % (by weight)
- Cl   51 % (by weight)
- OEt   1.2 % (by weight)
- OBu   10.8 % (by weight)
- Porosity (B.E.T.)   0.114 cm³/g, 50% thereof being due to pores with a radius of >0.026 μm (>260 Å)
- Surface Area (B.E.T.)   33 m²/g
- Porosity (mercury)   0.48 cm³/g due to pores with a radius of 0-to-1 μm (0-to-10,000 Å), 50% thereof being due to pores with a radius of >0.12 μm (>1,200 Å). Within the range of pores with a radius of 0-to-30 μm (0-to-300,000 Å), 55% of the pores had a radius of >1 μm (>10,000 Å).

Copolymerization of Ethylene with Butene-1 (LLDPE)

The copolymerization of ethylene with butene-1 was carried out under the same conditions as for Example 1. Using 0.092 g of the solid component, 280 g of polymer were obtained.

The characteristics of the polymer were as follows:

- MIE   0.6 g/10 min
- MIF/MIE   28
- Real Density   0.921 g/cm³
- Fraction Soluble in Xylene   7.3 %
- Bonded Butene   5.8 %
- Bulk Density, Poured   0.32 g/cm³
- Flowability   18 s
- Morphology   spherical

- P.S.D. >4,000 µm   <1 % (by weight)
          2,000-4,000 µm   30-40 % (by weight)
          1,000-2,000 µm   40-60 % (by weight)
          500-1,000 µm   1-3 % (by weight)
          <500 µm   <1 % (by weight)

Polymerization of Ethylene (HDPE)

The copolymerization of ethylene was carried out under the same conditions as for Example 1. At the end, 300 g of polymer were obtained, which exhibited the following characteristics:

- MIE   0.084 g/10 min
- MIF/MIE   27.9
- Bulk Density, Poured   0.33 g/cm^3
- Flowability   15 s
- Morphology   spherical
- P.S.D. >4,000 µm   <1 % (by weight)
          2,000-4,000   µm 20-30 % (by weight)
          1,000-2,000   ·µm 30-70 % (by weight)
          500-1,000   µm 1-3 % (by weight)
          <500 µm   <2 % (by weight)

EXAMPLE 3

The spherical support was prepared according to the general method and was subjected to thermal treatment until 45% of residual alcohol was obtained (molar ratio alcohol/ethanol = 1.7).

2,360 of this support, in suspension in 18 1 of anhydrous hexane, were charged to a 30 liter reactor. With stirring and at ambient temperature, 1,315 g of AlEt$_3$ in hexane solution (concentration 100 g/liter) were fed over 60 minutes. The temperature was raised to 60°C in 60 minutes, and kept constant for a further 60 minutes. The liquid phase was removed by settling and filtering and 15 liters of anhydrous hexanol were fed. The treatment was repeated two more times, operating under the same conditions. The spherical powder was washed 5 times with 10 liters of anhydrous hexane and vacuum dried.

The characteristics were as follows:

- Residual OEt   8.4 % (by weight)
- Cl   60.5 % (by weight)
- Mg   13.8 % (by weight)
- Morphology   spherical.

1,500 g of the so obtained support, in suspension with 17 liters of anhydrous hexane, were charged to a 25 liter reactor. With stirring and at ambient temperature, 2,750 g of Ti(OBu)$_4$ were fed. Stirring was continued at ambient temperature for 60 minutes and then 2,100 g of SiCl$_4$ were slowly added. The temperature was raised to 60°C and kept constant for 2 hours. A number of washes with anhydrous hexane was carried out to eliminate any free SiCl$_4$, with the very fine powder remaining

in suspension (approximately 1% by weight with a size of <5µm) being simultaneously removed from the solid component which was settling. The solid component was then vacuum dried at 50°C.

The characteristics were as follows:

- Total Titanium   6.7 % (by weight)
- Ti^{III} 4.3 % (by weight)
- Mg   11.5 % (by weight)
- Cl   52.3 % (by weight)
- OEt   1.9 % (by weight)
- OBu   13.4 % (by weight)
- Porosity (B.E.T.)   0.083 cm^3/g, 50% thereof being due to pores with a radius of >0.022 µm (>220 Å)
- Surface Area (B.E.T.)   24.3 m^2/g
- Porosity (mercury)   0.457 cm^3/g due to pores with a radius of 0-to-1 µm (0-to-10,000 Å), 50% thereof being due to pores with a radius of >0.12 µm (>1,200 Å). Within the range of pores with a radius of 0-to-30 µm (0-to-300,000 Å), 60% of the pores had a radius of >1 µm (10,000 Å).

Copolymerization of Ethylene with Butene-1 (LLDPE)

0.0114 g of the so obtained spherical component were used to copolymerize ethylene with butene-1 according to the same procedure as described in Example 1.

320 g of polymer were obtained, which had the following characteristics:

- MIE   1.5 g/10 min
- MIF/MIE   30
- Real Density   0.916 g/cm^3
- Fraction Soluble in Xylene   14 %
- Bonded Butene   7.7 %
- Bulk Density, Poured   0.33 g/cm^3
- Flowability   20 s
- Morphology   spherical
- P.S.D. >4,000 µm   <0.5 % (by weight)
          2,000-4,000 µm   20-30 % (by weight)
          1,000-2,000 µm   40-60 % (by weight)
          500-1,000 µm   2-4 % (by weight)
          <500 µm   <1 % (by weight)

EXAMPLE 4

A 1,000 cm^3 reactor was charged with 40 g of the support of Example 1, after having been treated with AlEt$_3$, in suspension with 500 cm^3 of anhydrous hexane. With stirring and at ambient temperature, 40 g of Ti(OC$_4$H$_9$)Cl$_3$ diluted in 100 cm^3 of hexane were fed. The temperature was raised to 55°C and kept constant for 1 hour. The liquid phase was removed, then the treatment was repeated with an additional 40 g of Ti(OC$_4$H$_9$)Cl$_3$ diluted with 300 cm^3 of hexane, at a temperature of 60°C for 2 hours. Thereafter, three washes were carried

out at 60°C and 4 washes at ambient temperature, each time using 300 cm³ of hexane.

After vacuum drying at 40°C, the solid powder in spherical form had the following characteristics:

- Total Titanium   5.4 % (by weight)
- Porosity (B.E.T.)   0.116 cm³/g, 50% thereof being due to pores with a radius of >0.03 μm (>300 Å)
- Surface Area (B.E.T.)   26.5 m²/g
- Porosity (mercury)   0.520 cm³/g due to pores with a radius of 0-to-1 μm (0-to-10,000 Å), 50% thereof being due to pores with a radius of >0.132 μm (>1,320 Å). Within the range of pores with a radius of 0-to-30 μm (0-to-300,000 Å), 52% of the pores had a radius of >1 μm (>10,000 Å).

Polymerization of Ethylene (HDPE)

The polymerization of ethylene was carried out under the same conditions as for Example 1, using 0.0093 g of the solid catalyst component. After a polymerization time of three hours, 320 g of polymer were obtained, which showed the following characteristics:

- MIE   0.413 g/10 min
- MIF/MIE   30.2
- Bulk Density, Poured   0.33 g/cm³
- Flowability   17 s
- Morphology   spherical
- P.S.D. >4,000 μm   <1 % (by weight)
  2,000-4,000 μm   30-50 % (by weight)
  1,000-2,000 μm   20-40 % (by weight)
  500-1,000 μm   3-5 % (by weight)
  <500 μm   <2 % (by weight)

EXAMPLE 5

A 1 liter reactor was charged with 50 g of the support of Example 1, after having been treated with AlEt₃, in suspension with 500 cm³ of hexane. With stirring and at ambient temperature, 13 g of Ti(OBu)₄ diluted with 50 cm³ of hexane were fed over 15 minutes. Stirring was continued for 1 hour, and then 20 g of SiCl₄ were fed over 15 minutes; thereafter the temperature was raised to 50°C and kept constant for 2 hours. Washes with hexane were carried out to eliminate any free SiCl₄, followed at the end by vacuum drying at 50°C.

The resulting catalyst component in spherical form exhibited the following characteristics:

- Total Titanium   2.7 % (by weight)
- Cl   57.4 % (by weight)
- OEt   5.6 % (by weight)
- OBu   10.5 % (by weight)
- Porosity (B.E.T.)   0.22 cm³/g, 50% thereof being due to pores with a radius of >0.03 μm (>300 Å)
- Porosity (mercury)   0.58 cm³/g due to pores

with a radius of 0-to-1 μm (0-to-10,000 Å), 50% thereof being due to pores with a radius of >0.125 μm (>1,250 Å). Within the range of pores with a radius of 0-to 30 μm (0-to-300,000 Å), 51.6% of the pores had a radius of >1 μm (>10,000 Å).

Polymerization of Ethylene (HDPE)

The polymerization was carried out under the same conditions as for Example 1, using 0.013 g of the solid, catalyst component. 215 g of polymer were obtained, which exhibited the following characteristics:

- MIE   0.153 g/10 min
- MIF/MIE   30
- Bulk Density, Poured   0.33 g/cm³
- Flowability   18 s
- Morphology   spherical
- P.S.D. >4,000 μm   <1 % (by weight)
  2,000-4,000 μm   20-30 % (by weight)
  1,000-2,000 μm   50-60 % (by weight)
  500-1,000 μm   2-4 % (by weight)
  <500 μm   <2 % (by weight)

EXAMPLE 6

Continuous Polymerization of Ethylene in the Gas phase to Obtain HDPE

1.14 g/hr of the catalyst prepared as in Example 2 was prepolymerized with ethylene, in continuous, in a reactor at 30°C, 10.0 g/hr of TEAL being fed.

The resulting prepolymer was continuously fed to a fluidized bed gas-phase reactor, kept at 80°C and 20 bars and having the following molar composition in the gas phase:

- Propane   77.2%
- Ethylene   12.3%
- Hydrogen   7.7%

(the balance to 100% was formed by inert gases).

An average yield of 6.23 Kg/g of catalyst was obtained, and the resulting polymer had the following characteristics:

- MIE   1.75 g/10 min
- MIF/MIE   28
- Real Density   0.960 g/cm³
- Bulk Density, Poured   0.400 g/cm³
- Bulk Density, Tamped   0.438 g/cm³
- Flowability   9 s
- Morphology   spherical
- P.S.D. >4,000 μm   0.0 % (by weight)
  2,000-4,000 μm   51.8 % (by weight)
  1,000-2,000 μm   43.9 % (by weight)
  500-1,000 μm   3.7 % (by weight)
  <500 μm   0.6 % (by weight)

EXAMPLE 7

Continuous Polymerization of Ethylene and Butene-1 to Obtain LLDPE

1.25 g/hr of the catalyst prepared as in Example 2 was prepolymerized with ethylene, in continuous, in a reactor at 30°C, 10.4 g/hr of TEAL being fed.

The resulting prepolymer was continuously fed to a fluidized bed gas-phase reactor, kept at 80°C and 20 bars and having the following molar composition in the gas phase:

- Propane   78.9%
- Ethylene   13.2%
- Butene-1   4.6%
- Hydrogen   2.1%

(the balance to 100% was formed by inert gases).

An average yield of 10.4 Kg/g of catalyst was obtained, and the resulting polymer had the following characteristics:

- MIE   1.01 g/10 min
- MIF/MIE   28.0
- Butene-1 Content   7.0 % by weight
- Fraction Soluble in Xylene   12.5 % by weight
- Real Density   0.919 g/cm^3
- Bulk Density, Poured   0.40 g/cm^3
- Bulk Density, Tamped   0.423 g/cm^3
- Melting Point   123.9 °C
- Flowability   12 s
- P.S.D. >4,000 μm   0.0 % (by weight)
      2,000-4,000 μm   55 % (by weight)
      1,000-2,000 μm   41.5 % (by weight)
      500-1,000 μm   3.0 % (by weight)
      <500 μm   0.5 % (by weight)

EXAMPLE 8

Step a)

In a 10 liter reactor equipped with a stirrer, 3,662 g of tetrabutoxytitanium were caused to react with 2,840 g of silicon tetrachloride. The reaction was conducted by adding the silicon tetrachloride to the tetrabutoxytitanium contained in the reactor, over a time period of 60 minutes and at ambient temperature. The temperature was then raised to 30°C and kept constant for an additional 60 minutes.

Step b)

A second 25 liter reactor, equipped with a stirrer, was charged with 2,000 g of the support of Example 1, after the treatment with AlEt$_3$, and 10 1 of anhydrous hexane.

At ambient temperature and over 60 minutes, the product resulting from Step a) was introduced into the reactor of Step b), containing the hexanol slurry of the support kept under agitation. The temperature was then raised to 60°C over a time period of 60 minutes and maintained constant for an additional 120 minutes.

The solid portion was allowed to settle and the liquid phase was removed, together with a small amount of a very fine TiCl$_3$ powder, by siphoning.

Thereafter the solid was washed seven consecutive times using 10 1 of wash grade anhydrous hexane each time, at ambient temperature, and then vacuum dried at about 40°C.

The resulting dry powder showed a spherical form and a good flowability and exhibited the following characteristics:

- Total Titanium   5.3 % (by weight)
- Ti^{III} 3.2 % (by weight)
- Mg   15.9 % (by weight)
- Cl   53.5 % (by weight)
- OEt   2.6 % (by weight)
- OBu   13 % (by weight)
- Porosity (B.E.T.)   0.122 cm^3/g, 50% thereof being due to pores with a radius of >0.01 μm (>100 Å)
- Porosity (mercury)

    - Total Porosity = 0.79 cm^3/g;
    - Porosity due to pores with a radius of from 0 to 1 μm (0 to 10,000 Å) = 0.453 cm^3/g, 50% thereof being due to pores with a radius of > 0.1 μm (>1,000 Å).

Polymerization of Ethylene (HDPE)

The polymerization was carried out using the same procedure as in Example 1, the only difference being that ethylene and hydrogen were fed at 40°C until a polymerization yield of about 50-100 g of polymer per g of the catalyst (prepolymerization step) was reached, and thereafter the temperature was raised to 75°C and maintained constant for 3 hours.

Using 0.0101 g of the solid catalyst component, 230 g of polymer were obtained. The characteristics of the polymer were as follows:

- MIE   4.38 g/10 min
- MIF/MIE   34.93
- Real Density   0.961 g/cm^3
- Bulk Density, Poured   0.355 g/cm^3
- Flowability   18 s
- Morphology   spherical

Copolymerization of Ethylene and Butene-1 (LLDPE)

The copolymerization was carried out according to the same procedure as in Example 1, using 0.118 of the spherical component obtained as indicated above, the only difference being that a short pre-polymerization

step at 40°C to reach a yield of about 50-100 g of polymer per g of the catalyst was carried out prior to raising the temperature to 75°C.

385 g of polymer were obtained, which showed the following characteristics:

- MIE   0.8 g/10 min
- MIF/MIE   . 29
- Fraction Soluble in Xylene   12 % by weight
- Real Density   0.9212 g/cm^3
- Bulk Density, Poured   0.330 g/cm^3
- Flowability   18 s
- Morphology   spherical
- P.S.D. >4,000 μm   <2 % (by weight)
      2,000-4,000 μm   49 % (by weight)
      1,000-2,000 μm   45.5 % (by weight)
      500-1,000 μm   2.8 % (by weight)
      <500 μm   <0.7 % (by weight)

EXAMPLE 9

Step a)

In a 50 cm^3 reactor, 12.5 g of the product of Ti (OBu)$_4$ + SiCl$_4$ were prepared under the same conditions as in Example 8, Step a).

Step b)

50 g of the support of Example 1, after having been treated with AlEt$_3$, were treated with dry air up to complete elimination of the residual C$_2$H$_5$ groups.

A 500 cm^3 reactor was charged with 150 cm^3 of anhydrous hexane and 50 g of the support obtained from Step b) above. Under stirring and at ambient temperature, 12.5 g of the product from Step a) above were fed to the reactor, over a time period of about 30 minutes. The temperature was raised to 60°C and kept constant for 2 hours. The solid portion was allowed to settle and the liquid phase was removed by siphoning. Seven washes each with 200 cm^3 of wash grade anhydrous hexane were carried out, by settling and siphoning, followed by vacuum drying at 40°C.

60 g of a dry powder having a spherical shape and good flowability was obtained, showing the following characteristics:

- Total Titanium   1.25 % (by weight)
- Ti^{III} 0.15 % (by weight)
- Mg   15.95 % (by weight)
- Cl   51.75 % (by weight)
- OEt   9.8 % (by weight)
- OBu   6.7 % (by weight)

Polymerization of Ethylene (HOPE)

The polymerization was carried out under the same conditions of Example 8, using 0.0098 g of the solid catalyst component. 215 g of polymer were obtained, which exhibited the following characteristics:

- MIE   2.88 g/10 min
- MIF/MIE   32.29
- Real Density   0.961 g/cm^3
- Bulk Density, Poured   0.34 g/cm^3
- Flowability   18 s
- Morphology   spherical
- P.S.D. >4,000 μm   <0.2 % (by weight)
      2,000-4,000 μm   38.8 % (by weight)
      1,000-2,000 μm   57.5 % (by weight)
      500-1,000 μm   2.9 % (by weight)
      <500 μm   <0.6 % (by weight)

Claims

1. Spherical components of catalysts for the polymerization of olefins comprising, supported on a magnesium dihalide in active form, a titanium compound containing at least one Ti-halogen bond and one OR group or OCOR group, wherein R is an alkyl, cycloalkyl or aryl radical of 1-18 carbon atoms, said OR group or OCOR group being bonded to Ti in such an amount as to yield molar ratios OR/Ti greater than or equal to 0.5, said components being characterized in that:

   - the porosity determined by mercury porosimetry is comprised within the range of from 0.35 to 0.7 cm^3/g; and
   - at least 50% of said porosity is due to pores having a radius greater than 0.08μm (800 Å).

2. Spherical components according to claim 1, characterized in that at least 30% of the total porosity is due to pores having a a radius greater than 1 μm (10,000 Å).

3. Spherical components according to claim 1, characterized by having a surface area comprised between 5 and 30 m^2/g.

4. Spherical components according to claim 1, characterized in that the magnesium dihalide in active form is MgCl$_2$.

5. Spherical components according to claim 1, characterized by comprising an electron donor compound.

6. Spherical components according to claim 1, characterized in that the titanium compound has the formula Ti(OR^l)$_n$X$_{y-n}$, wherein 0.5≤n≤(y-1), y is the valence of the titanium, X is halogen, and R^l is an alkyl radical having 2-8 carbon atoms.

7. Spherical components according to claim 6, wherein y is 4 and n varies within the range of from 1 to 2.

8. Spherical components according to claim 6, wherein X is chlorine.

9. Spherical components according to claim 6, wherein R is selected from n-butyl, isobutyl, 2-ethylhexyl, n-octyl, and phenyl.

10. Spherical components according to claim 5, wherein the electron donor compound is selected from alkyl, cycloalkyl, aryl ethers and esters of polycarboxylic acids.

11. Spherical components according to claim 1, characterized by being obtained by the reaction of:

(a) an $MgCl_2 \cdot pROH$ adduct, wherein $p \leq 0.5$ and R is an alkyl, cycloalkyl or aryl radical having 1-12 carbon atoms; with
(b) a titanium compound of the formula Ti $(OR)_n X_{y-n}$, wherein $0.5 \leq n \leq (y-1)$, y is the valence of the titanium, X is halogen, and R is an alkyl, cycloalkyl or aryl radical having 1-18 carbon atoms or a COR group;

said adduct (a) being prepared by chemical dealcoholation of adducts $MgCl_2 \cdot mROH$, with $m \leq 2$, in turn obtained by thermal dealcoholation of adducts $MgCl_2 \cdot qROH$ adduct, wherein $2.5 \leq q \leq 3.5$.

12. Spherical components according to claim 11, characterized in that in the reaction of the compound (b) with the adduct (a) the molar ratio Ti/Mg is comprised between 0.05 and 3.

13. Spherical components according to claim 11, characterized in that the compound (b) is a trichloroalkoxide of tetravalent titanium.

14. Spherical components according to claim 1, characterized by being obtained by the reaction of:

(a) an $MgCl_2 \cdot pROH$ adduct, wherein $p \leq 0.5$ and R is an alkyl, cycloalkyl or aryl radical having 1-12 carbon atoms; with
(b) a titanium compound of the formula Ti $(OR)_n X_{4-n}$ or $Ti(OCOR)_n X_{4-n}$, wherein $0 \leq n \leq 2$, X is halogen and R is an alkyl, cycloalkyl or aryl radical having 1-18 carbon atoms;

said adduct (a) being prepared by chemical dealcoholation of adducts $MgCl_2 \cdot mROH$, with $m \leq 2$, in turn obtained by thermal dealcoholation of adducts $MgCl_2 \cdot qROH$, wherein $2.5 \leq q \leq 3.5$.

15. Spherical components according to claim 14, characterized in that the reaction is conducted in the presence of a compound ROH, where R is an alkyl, cycloalkyl or aryl radical having 1-12 carbon atoms.

16. Spherical components according to claim 14, characterized in that the reaction is conducted in the presence of a reducing compound.

17. Spherical components according to claim 14, characterized in that in the reaction the molar ratio of the titanium present in the compound (b) to the magnesium present in the adduct (a) varies within the range of from 0.05 to 3.

18. Spherical components according to claim 14, characterized in that the compound (b) is $TiCl_4$ or Ti(OR) Cl_3.

19. Spherical components according to claim 1, characterized by being obtained by the reaction of:

(a) an $MgCl_2 \cdot pROH$ adduct, wherein $p \leq 0.5$ and R is an alkyl, cycloalkyl or aryl radical having 1-12 carbon atoms; with
(b) a titanium compound of the formula Ti $(OR)_n X_{4-n}$ or $Ti(OCOR)_n X_{4-n}$, wherein $2 \leq n \leq 4$, X is halogen and R is an alkyl, cycloalkyl or aryl radical having 1-18 carbon atoms; and
(c) a halogenating compound, optionally in combination with a reducing compound, or a compound having both a halogenating and a reducing activity;

said adduct (a) being prepared by chemical dealcoholation of adducts $MgCl_2 \cdot mROH$, with $m \leq 2$, in turn obtained by thermal dealcoholation of adducts $MgCl_2 \cdot qROH$, wherein $2.5 \leq q \leq 3.5$.

20. Spherical components according to claim 17, characterized in that in the reaction the molar ratio of the titanium present in the compound (b) to the magnesium present in the adduct (a) varies within the range of from 0.05 to 3.

21. Spherical components according to claim 17, characterized in that the compound (b) is $Ti(OR)_4$.

22. Catalysts for the polymerization of olefins $CH_2=CHR$, wherein R is hydrogen or an alkyl, cycloalkyl or aryl group having from 1 to 8 carbon atoms, characterized by comprising the product of the reaction of the spherical components according to claim 1 and an Al-alkyl compound.

23. Catalysts according to claim 22, wherein the Al-alkyl compound is an Al-trialkyl compound.

24. Process for the polymerization of ethylene and mixtures thereof with the olefins $CH_2=CHR$, wherein R is an alkyl, cycloalkyl or aryl group having 1-12 carbon atoms, optionally in the presence of minor amounts of a diene, characterized by comprising

the use of the catalysts according to claim 22.

25. Process according to claim 24, characterized in that the olefin $CH_2=CHR$ is selected from butene-1, pentene-1, hexene-1, 4-methyl-pentene-1, and octene-1.

Patentansprüche

1. Kugelförmige Katalysatorkomponenten zur Polymerisation von Olefinen, umfassend, getragen auf einem Magnesiumdihalogenid in aktiver Form, eine Titanverbindung, die mindestens eine Ti-Halogen-Bindung und eine Gruppe OR oder Gruppe OCOR enthält, worin R einen Alkyl-, Cycloalkyl- oder Arylrest mit 1-18 Kohlenstoffatomen darstellt, wobei die Gruppe OR oder Gruppe OCOR an Ti in einer solchen Menge gebunden ist, daß Molverhältnisse OR/Ti größer als oder gleich 0,5 erhalten werden, wobei die Komponenten dadurch gekennzeichnet sind, daß:

   - die Porosität, bestimmt durch Quecksilberporosimetrie, im Bereich von 0,35 bis 0,7 cm^3/g umfaßt ist;
   - und mindestens 50% der Porosität von Poren mit einem Radius größer als 0,08 μm (800 Å) stammen.

2. Kugelförmige Komponenten nach Anspruch 1, dadurch gekennzeichnet, daß mindestens 30% der Gesamtporosität von Poren mit einem Radius größer als 1 μm (10000 Å) stammen.

3. Kugelförmige Komponenten nach Anspruch 1, gekennzeichnet durch eine Oberfläche, umfaßt zwischen 5 und 30 m^2/g.

4. Kugelförmige Komponenten nach Anspruch 1, dadurch gekennzeichnet, daß das Magnesiumdihalogenid in aktiver Form $MgCl_2$ ist.

5. Kugelförmige Komponenten nach Anspruch 1, dadurch gekennzeichnet, daß sie eine Elektronendonorverbindung umfassen.

6. Kugelförmige Komponenten nach Anspruch 1, dadurch gekennzeichnet, daß die Titanverbindung die Formel $Ti(OR^l)_nX_{y-n}$ aufweist, worin $0,5 \leq y \leq (y-1)$, y die Wertigkeit von Titan ist, X Halogen darstellt und R^l einen Alkylrest mit 2-8 Kohlenstoffatomen darstellt.

7. Kugelförmige Komponenten nach Anspruch 6, wobei y 4 ist und n im Bereich 1 bis 2 liegt.

8. Kugelförmige Komponenten nach Anspruch 6, wobei X Chlor darstellt.

9. Kugelförmige Komponenten nach Anspruch 6, wobei R ausgewählt ist aus n-Butyl, Isobutyl, 2-Ethylhexyl, n-Octyl und Phenyl.

10. Kugelförmige Komponenten nach Anspruch 5, wobei die Elektronendonorverbindung ausgewählt ist aus Alkyl-, Cycloalkyl-, Arylethern und -estern von Polycarbonsäuren.

11. Kugelförmige Komponenten nach Anspruch 1, dadurch gekennzeichnet, daß sie erhalten werden durch die Reaktion von:

   (a) einem $MgCl_2 \cdot pROH$-Addukt, worin $p \leq 0,5$ und R einen Alkyl-, Cycloalkyl- oder Arylrest mit 1-12 Kohlenstoffatomen darstellt; mit
   (b) einer Titanverbindung der Formel $Ti(OR)_nX_{y-n}$, worin $0,5 \leq n \leq (y-1)$, y die Wertigkeit des Titans darstellt, X Halogen darstellt und R einen Alkyl-, Cycloalkyl- oder Arylrest mit 1-18 Kohlenstoffatomen oder eine Gruppe COR darstellt;

   wobei das Addukt (a) hergestellt wird durch chemische Entalkoholisierung von Addukten $MgCl_2 \cdot mROH$ mit $m \leq 2$, wiederum erhalten durch thermische Entalkoholisierung von Addukten $MgCl_2 \cdot qROH$, worin $2,5 \leq q \leq 3,5$.

12. Kugelförmige Komponenten nach Anspruch 11, dadurch gekennzeichnet, daß bei der Reaktion der Verbindung (b) mit dem Addukt (a) das Molverhältnis Ti/Mg zwischen 0,05 und 3 umfaßt wird.

13. Kugelförmige Komponenten nach Anspruch 11, dadurch gekennzeichnet, daß die Verbindung (b) ein Trichloralkoxid von vierwertigem Titan darstellt.

14. Kugelförmige Komponenten nach Anspruch 1, dadurch gekennzeichnet, daß sie erhalten werden durch die Reaktion von:

   (a) einem $MgCl_2 \cdot pROH$-Addukt, worin $p \leq 0,5$ und R einen Alkyl-, Cycloalkyl- oder Arylrest mit 1-12 Kohlenstoffatomen darstellt; mit
   (b) einer Titanverbindung der Formel $Ti(OR)_nX_{4-n}$ oder $Ti(OCOR)_nX_{4-n}$, worin $0 \leq n \leq 2$, X Halogen darstellt und R einen Alkyl-, Cycloalkyl- oder Arylrest mit 1-18 Kohlenstoffatomen darstellt,

   wobei das Addukt (a) hergestellt wird durch chemische Entalkoholisierung von Addukten $MgCl_2 \cdot mROH$ mit $m \leq 2$, wiederum erhalten durch thermische Entalkoholisierung von Addukten $MgCl_2 \cdot qROH$, worin $2,5 \leq q \leq 3,5$.

15. Kugelförmige Komponenten nach Anspruch 14, dadurch gekennzeichnet, daß die Reaktion in Gegenwart einer Verbindung ROH, worin R einen Alkyl-, Cycloalkyl- oder Arylrest mit 1-12 Kohlenstoffatomen darstellt, durchgeführt wird.

16. Kugelförmige Komponenten nach Anspruch 14, dadurch gekennzeichnet, daß die Reaktion in Gegenwart einer reduzierenden Verbindung durchgeführt wird.

17. Kugelförmige Komponenten nach Anspruch 14, dadurch gekennzeichnet, daß bei der Reaktion das Molverhältnis des in der Verbindung (b) vorliegenden Titans zu in dem Addukt (a) vorliegendem Magnesium im Bereich von 0,05 bis 3 liegt.

18. Kugelförmige Komponenten nach Anspruch 14, dadurch gekennzeichnet, daß die Verbindung (b) $TiCl_4$ oder $Ti(OR)Cl_3$ darstellt.

19. Kugelförmige Komponenten nach Anspruch 1, dadurch gekennzeichnet, daß sie erhalten werden durch die Reaktion von:

(a) einem $MgCl_2 \cdot pROH$-Addukt, worin $p \le 0,5$ und R einen Alkyl-, Cycloalkyl- oder Arylrest mit 1-12 Kohlenstoffatomen darstellt; mit
(b) einer Titanverbindung der Formel $Ti(OR)_nX_{4-n}$ oder $Ti(OCOR)_nX_{4-n}$, worin $2 \le n \le 4$, X Halogen darstellt und R einen Alkyl-, Cycloalkyl- oder Arylrest mit 1-18 Kohlenstoffatomen darstellt; und
(c) einer halogenierenden Verbindung, gegebenenfalls in Kombination mit einer reduzierenden Verbindung oder einer Verbindung mit sowohl halogenierender, als auch reduzierender Wirkung;

wobei Addukt (a) hergestellt wird durch chemische Entalkoholisierung von Addukten $MgCl_2 \cdot mROH$ mit $m \le 2$, wiederum erhalten durch thermische Entalkoholisierung von Addukten $MgCl_2 \cdot qROH$, worin $2,5 \le q \le 3,5$.

20. Kugelförmige Komponenten nach Anspruch 17, dadurch gekennzeichnet, daß in der Reaktion das Molverhältnis des in der Verbindung (b) vorliegenden Titans zu in dem Addukt (a) vorliegendem Magnesium im Bereich von 0,05 bis 3 liegt.

21. Kugelförmige Komponenten nach Anspruch 17, dadurch gekennzeichnet, daß die Verbindung (b) $Ti(OR)_4$ darstellt.

22. Katalysatoren zur Polymerisation von Olefinen $CH_2=CHR$, worin R Wasserstoff oder eine Alkyl-, Cycloalkyl- oder Arylgruppe mit 1 bis 8 Kohlenstoff- atomen darstellt, dadurch gekennzeichnet, daß sie das Reaktionsprodukt der kugelförmigen Komponenten nach Anspruch 1 und einer Al-Alkyl-Verbindung umfassen.

23. Katalysatoren nach Anspruch 22, wobei die Al-Alkyl-Verbindung eine Al-Trialkyl-Verbindung darstellt.

24. Verfahren zur Polymerisation von Ethylen und dessen Gemischen mit Olefinen $CH_2=CHR$, worin R eine Alkyl-, Cycloalkyl- oder Arylgruppe mit 1-12 Kohlenstoffatomen darstellt, gegebenenfalls in Gegenwart geringer Mengen eines Diens, dadurch gekennzeichnet, daß es die Verwendung von Katalysatoren nach Anspruch 22 umfaßt.

25. Verfahren nach Anspruch 24, dadurch gekennzeichnet, daß das Olefin $CH_2=CHR$ ausgewählt ist aus Buten-1, Penten-1, Hexen-1, 4-Methylpenten-1 und Octen-1.

Revendications

1. Constituants sphériques de catalyseurs pour la polymérisation d'oléfines comprenant, supporté sur un dihalogénure de magnésium sous forme active, un dérivé de titane comportant au moins une liaison Ti-halogène et un groupe OR, ou un groupe OCOR, où R est un radical alkyle, cycloalkyle ou aryle comportant 1 à 18 atomes de carbone, ledit groupe OR ou groupe OCOR étant lié au Ti en une quantité telle qu'on obtienne des rapports molaires OR/Ti supérieurs ou égaux à 0,5, lesdits constituants étant caractérisés en ce que :

- la porosité, déterminée par porosimétrie au mercure, est comprise dans la fourchette de 0,35 à 0,7 cm^3/g ; et
- au moins 50% de ladite porosité est due à des pores ayant un rayon supérieur à 0,08μm (800 A).

2. Constituants sphériques selon la revendication 1 caractérisés en ce qu'au moins 30% de la porosité totale est due à des pores ayant un rayon supérieur à 1μm (10 000 A).

3. Constituants sphériques selon la revendication 1, caractérisés en ce qu'ils présentent une surface spécifique comprise entre 5 et 30 m^2/g.

4. Constituants sphériques selon la revendication 1, caractérisés en ce que le dihalogénure de magnésium sous forme active est $MgCl_2$.

5. Constituants sphériques selon la revendication 1,

caractérisé en ce qu'ils comprennent un composé donneur d'électrons.

6. Constituants sphériques selon la revendication 1, caractérisés en ce que le dérivé de titane répond à la formule $Ti(OR^I)_nX_{y-n}$, où $0,5 \leq n \leq (y-1)$, y est la valence du titane, X est un halogène, et R^1 est un radical alkyle comprenant de 2 à 8 atomes de carbone.

7. Constituants sphériques selon la revendication 6, où y est égal à 4 et n varie dans la fourchette de 1 à 2.

8. Constituants sphériques selon la revendication 6, où X est le chlore.

9. Constituants sphériques selon la revendication 6, où R est choisi parmi n-butyle, isobutyle, 2-éthyl-hexyle, n-octyle, et phényle.

10. Constituants sphériques selon la revendication 5, où le composé donneur d'électrons est choisi parmi les alkyl, cycloalkyl, aryléthers et esters d'acides polycarboxyliques.

11. Constituants sphériques selon la revendication 1, caractérisés en ce qu'on les obtient par la réaction de :

(a) un adduct $MgCl_2.pROH$, où $p \leq 0,5$ et R est un radical alkyle, cycloalkyle ou aryle comportant 1 à 12 atomes de carbone ; avec
(b) un dérivé de titane de formule $Ti(OR)_nX_{y-n}$, où $0,5 \leq n \leq (y-1)$, y est la valence de titane, X est un halogène et R est un radical alkyle, cycloalkyle ou aryle comportant 1 à 18 atomes de carbone ou un groupe COR ;

ledit adduct (a) étant obtenu par désalcoolisation chimique des adducts $MgCl_2.mROH$, avec $m \leq 2$, eux-mêmes obtenus par désalcoolisation thermique des adducts $MgCl_2.qROH$, où $2,5 \leq q \leq 3,5$.

12. Constituants sphériques selon la revendication 11, caractérisés en ce que, dans la réaction du dérivé (b) avec l'adduct (a), le rapport molaire Ti/Mg est compris entre 0,05 et 3.

13. Constituants sphériques selon la revendication 11, caractérisés en ce que le dérivé (b) est un trichloroalcoolate de titane tétravalent.

14. Constituants sphériques selon la revendication 1, caractérisés en ce qu'on les obtient par la réaction de :

(a) un adduct $MgCl_2.pROH$, où $p \leq 0,5$ et R est un radical alkyle. cycloalkyle ou aryle comportant 1 à 12 atomes de carbone ; avec
(b) un dérivé de titane de formule $Ti(OR)_nX_{4-n}$ ou $Ti(OCOR)_nX_{4-n}$, où $0 \leq n \leq 2$, X est un halogène et R est un radical alkyle, cycloalkyle ou aryle comportant à à 1 atomes de carbone ;

ledit adduct (a) étant obtenu par désalcoolisation chimique des adducts $MgCl_2.mROH$, avec $m \leq 2$, eux-mêmes obtenus par désalcoolisation thermique des adducts $MgCl_2.qROH$ où $2,5 \leq q \leq 3,5$.

15. Constituants sphériques selon la revendication 14, caractérisés en ce qu'on effectue la réaction en présence d'un composé ROH, où R est un radical alkyle, cycloalkyle ou aryle comportant 1 à 12 atomes de carbone.

16. Constituants sphériques selon la revendication 14, caractérisés en ce qu'on effectue la réaction en présence d'un composé réducteur.

17. Constituants sphériques selon la revendication 14, caractérisés en ce que dans la réaction, le rapport molaire du titane présent dans le dérivé (b) au magnésium présent dans l'adduct (a) varie dans la fourchette de 0,05 à 3.

18. Constituants sphériques selon la revendication 14, caractérisés en ce que le dérivé (b) est $TiCl_4$ ou $Ti(OR)Cl_3$.

19. Constituants sphériques selon la revendication 1, caractérisés en ce qu'on les obtient par la réaction de :

(a) un adduct $MgCl_2.pROH$, où $p \leq 0,5$ et R est un radical alkyle, cycloalkyle ou aryle comportant 1 à 12 atomes de carbone ; avec
(b) un dérivé de titane de formule $Ti(OR)_nX_{4-n}$ ou $Ti(OCOR)_nX_{4-n}$ où $2 \leq n \leq 4$, X est un halogène et R est un radical alkyle, cycloalkyle ou aryle comportant 1 à 18 atomes de carbone ; et
(c) un composé halogénant, éventuellement en combinaison avec un composé réducteur ou un composé ayant à la fois une activité halogénante et réductrice ; ledit adduct (a) étant obtenu par désalcoolisation chimique des adducts $MgCl_2.mROH$, avec $m \leq 2$, eux-mêmes obtenus par désalcoolisation thermique des adducts $MgCl_2.qROH$, où $2,5 \leq q \leq 3,5$.

20. Constituants sphériques selon la revendication 17, caractérisés en ce que dans la réaction, le rapport molaire de titane présent dans le dérivé (b) au magnésium présent dans l'adduct (a) varie dans la fourchette de 0,05 à 3.

21. Constituants sphériques selon la revendication 17, caractérisés en ce que le dérivé (b) est $Ti(OR)_4$.

22. Catalyseurs pour la polymérisation d'oléfines $CH_2=CHR$, où R est l'hydrogène ou un groupe alkyle, cycloalkyle ou aryle comportant de 1 à 8 atomes de carbone, caractérisés en ce qu'ils comprennent le produit de la réaction des constituants sphériques selon la revendication 1 et un dérivé alkyl-Al.

23. Catalyseurs selon la revendication 22, dans lequel le dérivé alkyl-Al est un dérivé trialkyl-Al.

24. Procédé de polymérisation d'éthylène et de mélanges de celui-ci avec des oléfines $CH_2=CHR$, où R est un groupe alkyle, cycloalkyle ou aryle comportant 1 à 12 atomes de carbone, éventuellement en présence de quantités mineures d'un diène, caractérisé en ce qu'il comprend l'utilisation de catalyseurs selon la revendication 22.

25. Procédé selon la revendication 24, caractérisé en ce que l'oléfine $CH_2=CHR$ est choisie parmi butène-1, pentène-1, hexène-1, 4-méthyl-pentène-1 et octène-1.